

Synthesis and Characterization of Palm-Based Resin for UV Coating

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ABSTRACT: The production of UV curable acrylated polyol ester prepolymer from palm oil and its downstream products offer potential and promising materials for applications such as polymeric film preparation and coatings. In this study, palm olein polyol was reacted with acrylic acid in the presence of a catalyst and inhibitors via condensation esterification process. The reaction temperature of 80°C and the stirring rate of 400 rpm produce a homogeneous product. Based on iodine value result, the suitable amount of *p*-toluene sulfonic acid monohydrate used as catalyst was 3.0% (w/w) of palm olein polyol. Different UV curable formulations have been investigated using the synthesized prepolymers with monomers and a small amount of photoinitiator. Monomers used were 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacry-

late (TMPTA) while photoinitiator used was 1-hydroxy cyclohexyl phenylketone (Irgacure 184). The mixtures were cured to make thin polymeric films under UV radiation with doses between 2 and 14 passes (energy per pass is 0.6 J/cm²). Coating and curing was carried out on glass for pendulum hardness and FTIR analysis. Pendulum hardness of the film prepared using monomer HDDA and the prepolymer previously synthesized using 3.0% catalyst was 24.5%. The radiation dose needed was 14 passes. The highest pendulum hardness of 49.4% was achieved using monomer TMPTA and the prepolymer synthesized using 2.0% catalyst. The radiation dose needed was 10 passes. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2353–2361, 2009

Key words: palm-based resin; prepolymer; UV coating

INTRODUCTION

The development of new radiation curable resins, which can offer improved technical and economic performances, has generated a considerable research interest both in academic and industrial laboratories. It is always desirable to develop new chemicals out of natural products of renewable sources. Majority of the commercially available resins for surface coating are products of nonrenewable petroleum-based synthetic raw materials. Natural fats and oils are also used in industrial products. Linseed, castor, fish, soya, safflower, sunflower, and tall oils have been used in oleoresinous production. The types of coatings that may be formulated from oleoresinous are clear varnishes, industrial enamels, printing inks, epoxy paints, undercoats, and primers.¹ Palm oil holds very promising potential to be the next renewable raw material substitutes for industrial chemicals including radiation curable resins. The development of new radiation-curable materials for applications

such as wood and plastics coatings, printing ink, digital video disk (DVD) printing, pressure sensitive adhesive (PSA), electronic industries are most important research areas.²

Presently, most palm oil-based product for UV-curable coating is prepared from epoxidized palm oil (EPO); e.g., EPO and cycloaliphatic diepoxide are cured by UV radiation induced by cationic photoinitiator.³ Radiation curable acrylates can be derived from epoxidized oils by reacting them with acrylic acid.⁴ Epoxidized palm olein acrylate (EPOLA) had been prepared using EPO, acrylic acid, triethylamine as catalyst, and 4-methoxyphenol as gelling inhibitor.⁵ The potential application of EPOLA is radiation curable pressure sensitive adhesives (PSA).^{6,7} Another invention for radiation curable product was palm oil-based acrylated polyester resins, from crude or refined, bleached, and deodorized palm oil. Either one of these when incorporated with TMPTA or HDDA monomers was found to be most suitable for wood coating application.⁸

Vegetable oil-based polyol is produced by treating epoxidized oil with polyhydric alcohols.^{9,10} The objectives of this study are to prepare acrylated polyol ester prepolymer from polycondensation esterification between polyol and acrylic acid (Fig. 1) and thereafter to produce radiation curable formulation

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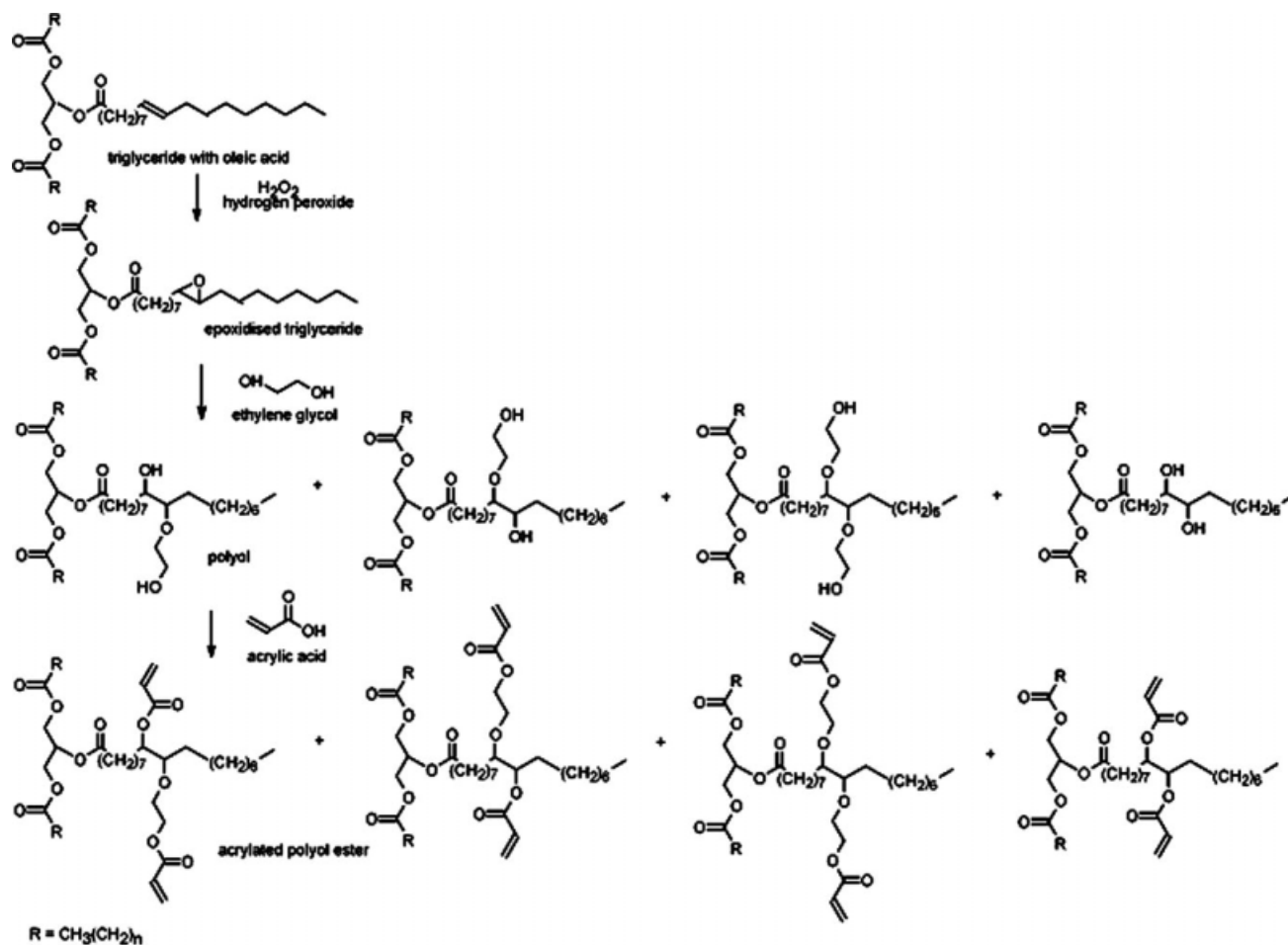


Figure 1 Reaction pathway of acrylated polyol ester prepolymer synthesis.

from the prepolymer. The acrylated polyol ester prepolymer was mixed with monomer of either 1,6-hexanediol diacrylate (HDDA) or trimethylolpropane triacrylate (TMPTA) while the photoinitiator used was 1-hydroxy cyclohexyl phenylketone (Irgacure 184) to produce radiation curable formulation. The formulation was applied on glass panel and cured under UV light.

In this study, the catalyst used for esterification purpose was *p*-toluene sulfonic acid monohydrate. Concentrated sulfuric acid, H_2SO_4 , could also be used but it gave lower yield and darker color product. The catalyst, *p*-toluene sulfonic acid monohydrate is a reactive esterification catalyst and is chosen for at least two purposes. First, this catalyst enables reaction at lower temperature as to reduce the possibility of thermally induced free radical reaction of the products. Second, this catalyst reduces reaction time and suppresses unwanted side reaction.¹¹

Inhibitors play an important role in preventing gelation throughout the esterification process. Gelation is a common phenomenon during the synthesis as a result of self-polymerization of reactant(s) containing

more than two functional groups per molecule.^{12,13} The most common inhibitors that are used for prevention of any unexpected polymerization reaction or gelling are hydroquinone, methoxy methyl hydroquinone, phenothiazene, *p*-benzoquinone, etc. Inhibitor is necessary to hinder thermally induced free radical polymerization reaction during synthesis process and prolongs storage.^{14,15}

In this synthesis, the polyacrylic acid may be formed, acrylic acid is a very reactive monomer and readily undergoes self-polymerization even at room temperature. Unsaturated vinyl group in the molecule in acrylic acid easily undergoes radical addition polymerization to yield a gel or network during synthesis.¹⁶ A sufficient amount of inhibitors must be added to the reactants to prevent the occurrence of such polymerization. Inhibitors used in the synthesis are a combination of 4-methoxyphenol and hydroquinone. They are chosen because of their differing mechanism in curbing gelation. 4-Methoxyphenol acts as a protecting group for primary alcohols.¹⁷ Oxygen in air and 4-methoxyphenol together give a synergistic inhibition of polymerization as illustrated in Figure 2. In the mechanism, R^* is a radical.

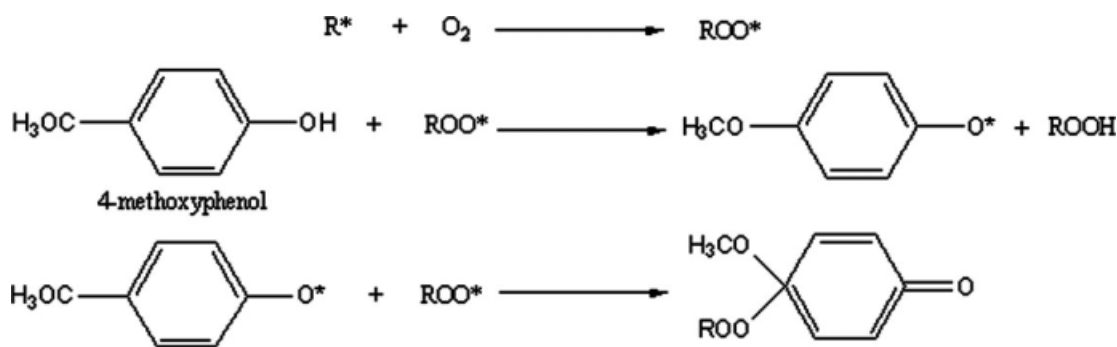


Figure 2 Mechanism of inhibition of polymerization by 4-methoxyphenol.

Hydroquinone is used because it does not give any color to either the reaction mixture or the final product. Figure 3 shows the mechanism involved during inhibition of polymerization by hydroquinone. The equations have shown that the antioxidant supplies hydrogen atoms to terminate both the initiating and propagating steps in the autoxidation chain reaction.¹⁸

Some researchers^{19,20} observed that the photoinitiator Irgacure 184 at 4% (w/w) concentration exhibited the best pendulum hardness than other photoinitiators available commercially. The simple structural augmentation of Irgacure 184 and its linear molecular geometry could be the other reasons why the small free radical entities can form easily to undergo free radical polymerization reaction in combination with the prepolymer and monomer unit. This may also be due to its easy free radical (benzoyl radical) formation and its affinity to undergo faster photoinduced free radical polymerization reaction.²¹

EXPERIMENTAL

Materials

Palm olein polyol was obtained from a polyol pilot plant at Advanced Oleochemical Technology Divi-

sion (AOTD) of Malaysian Palm Oil Board (MPOB). Acrylic acid was supplied by Merck, Germany. *p*-Toluene sulfonic acid monohydrate from Fluka Chemicals was used as a catalyst. Inhibitors, hydroquinone, and hydroquinone monomethyl ether were obtained from Fluka Chemicals. Toluene was supplied by Fisher Chemicals. Polyester acrylate oligomer (CN 2298) was supplied by Sartomer Company. Monomers, HDDA and TMPTA, were supplied by UCB Asia Pacific Sdn. Bhd. Photoinitiator, 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184), was supplied by Ciba Specialty Chemicals.

Preparation of acrylated polyol ester prepolymer

Palm olein polyol (300.0 g), acrylic acid with 30% excess (110.2 g), toluene as solvent (120.0 g), catalyst: 1.0, 2.0, 3.0, 4.0, or 5.0% (w/w) of palm olein polyol and inhibitors were placed in a five-necked reactor flask, equipped with thermometer, mechanical stirrer, and Dean and Stark apparatus to collect water from the synthesis. The top portion of Dean and Stark apparatus was fitted together with Liebig condenser and topped off with respirator pump to maintain mild vacuum condition in the reaction. The mixture in the flask was then heated to chosen

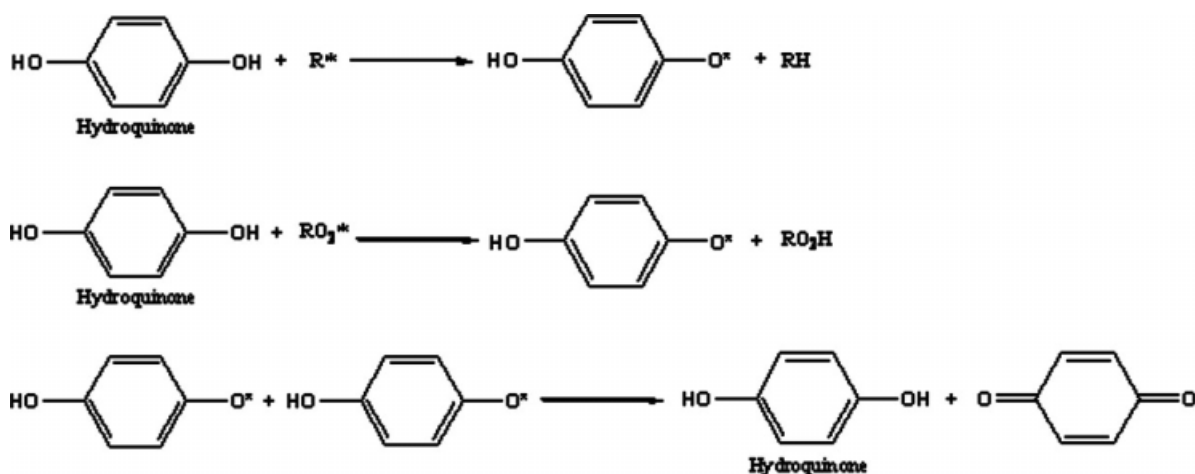


Figure 3 Mechanism of inhibition of polymerization by hydroquinone.

TABLE I
Formulation and Their Ratios of Acrylated Polyol Ester Prepolymer (Oligomer), Monomer, and Photoinitiator

Acrylated polyol ester prepolymer [Oligomer (O)] synthesized using % catalyst	Monomer (M)	Photoinitiator (P)	Ratio O : M : P (% w/w)
1.0	HDDA	Irgacure 184	50 : 46 : 4
2.0			
3.0			
4.0			
5.0			
1.0	TMPTA		
2.0			
3.0			
4.0			
5.0			

temperature (70.0, 80.0, 90.0, or 100.0°C) using oil bath. The mechanical stirrer was maintained at 400 rpm. The reaction was monitored by measuring acid and hydroxyl values every hourly for 15 h. After synthesis, unreacted acrylic acid and *p*-toluene sulfonic acid monohydrate were removed through water base extraction and petroleum ether (boiling point: 60–80°C). Synthesized acrylated polyol ester prepolymer then undergoes rotary evaporator to remove excessive petroleum ether.

Characterization of synthesized prepolymer

AOCS Official Method Te 2a-64 was used to measure acidity, whereas AOCS Official Method Cd 13-60 (pyridine-acetic anhydride titration method) was used to determine the hydroxyl value. Iodine value was determined by cyclohexane-acetic acid method according to AOCS Official Method Cd 1d-92. Fourier Transform Infrared (FTIR) spectra was recorded by Nicolet, Magna-IR 550 Spectrophotometer, Series II, USA. FTIR spectra were obtained by coating the samples on potassium bromide (KBr) pellet. Viscos-

ity was measured on a Brookfield Rheometer, Brookfield DV-III+ Calculating Digital Viscometer, using CP51 cylindrical spindle at 25°C. Gel permeation chromatographic (GPC) analysis was carried out on Tosoh made Model HLC-8020 using column 5 μm or 250 Å, 30 cm P.

Preparation and UV curing of coating

Formulations were developed using the acrylated polyol ester prepolymer incorporated with different monomers (shown in Table I). The coating formulations were prepared 1 day before curing and the containers were wrapped in black paper. The formulated solution was coated on clean glass plate (100 mm × 100 mm × 3 mm) by using a bar coater (RDS 20, Japan) and cured under UV lamp (2 kW; type of lamp: MC200; wavelength range: 180–450 nm) using IST UV machine (U-200M-1-Tr, Germany). The coated plate was irradiated up to 14 passes under a UV lamp at a conveyor speed of 4 m/min to achieve maximum crosslinking. The current supply was ~ 8 Å, of which energy given per pass was ~ 0.6 J/cm².

Characterization of UV cured coating by FTIR and pendulum hardness

FTIR spectra of irradiated samples were recorded by Perkin-Elmer Fourier Transform Infrared Spectrometer Model 842, USA with Golden Gate Single Reflection Diamond Attenuated Total Reflectance (ATR) D/N 10500 Series attached. Scanning was done by using UV cured film type sample (4 cm × 4 cm). The pendulum hardness of the UV-cured polymeric films was measured by a pendulum hardness tester, Model BYK Labotron, Germany. The procedure used was in accordance to ASTM Designation D-4366-87 Standard Test Methods for hardness of organics coatings by pendulum damping tests (Test method A—König pendulum hardness test). It is the number of oscillations made by the pendulum to reduce its angle of swing from 6° to 3°. The result is expressed as percentage pendulum hardness (% P. H.) given by:

$$\% \text{ P.H.} = \frac{\text{No. of oscillations for damping from } 6^\circ \text{ to } 3^\circ \text{ for sample}}{\text{No. of oscillations for damping from } 6^\circ \text{ to } 3^\circ \text{ for standard glass}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Analysis of synthesized prepolymer

Acrylated polyol ester prepolymer formation through interaction between hydroxyl group of palm olein polyol and acrylic acid was monitored by measuring the acid value every hourly. The reaction was conducted at relatively low temperatures, 70.0, 80.0, 90.0, or 100.0°C, as to reduce the formation of

polyacrylic acid which can solidify or gelled. Low temperature was also utilized to reduce evaporation of toluene and acrylic acid used in the system, which have the boiling point of 111 and 141°C, respectively. From Figure 4, the decrement of the acid value or acrylic acid indicated ester formation. At continuous and prolonged reaction period, the amount of acrylated polyol ester prepolymer produced is greater as there is more conversion from

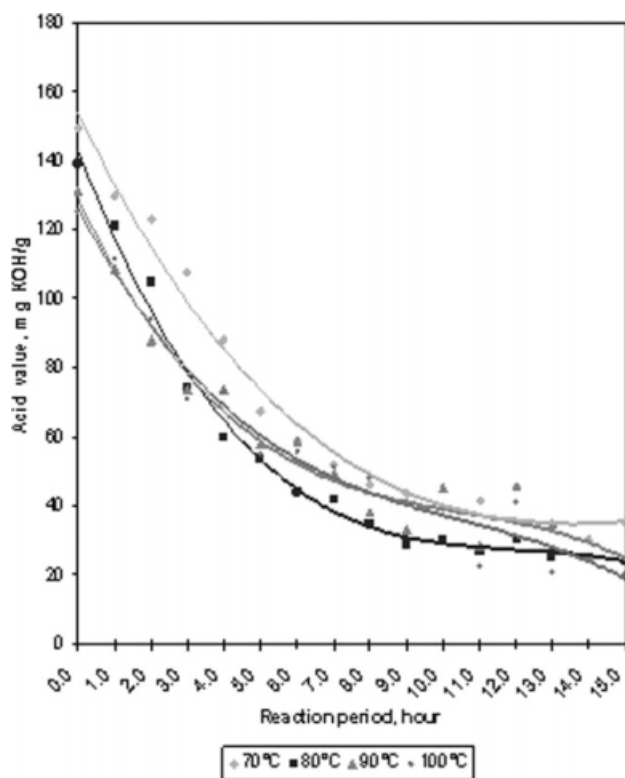


Figure 4 Effect of reaction period on the acid value. Other reaction conditions: temperature (70.0, 80.0, 90.0, or 100.0°C), catalyst concentration (5.0%), and stirring rate (400 rpm).

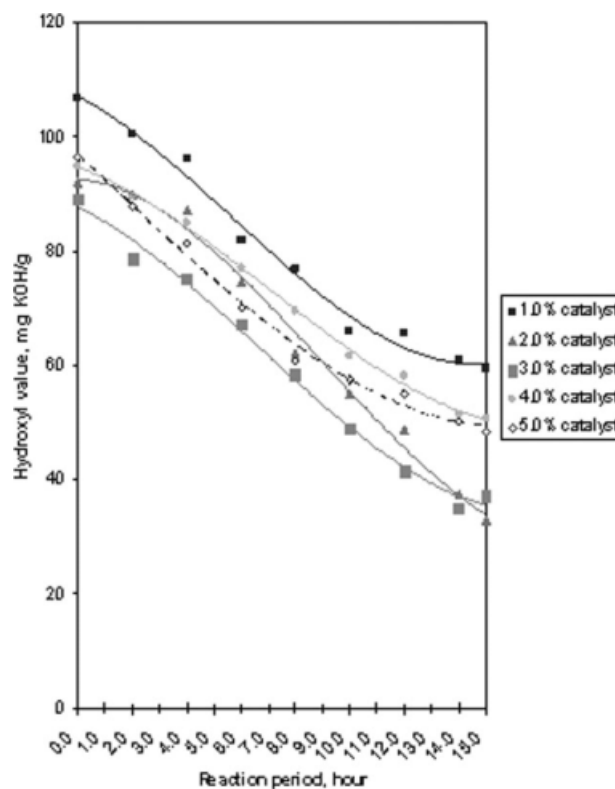


Figure 5 Effect of reaction period on the hydroxyl value. Other reaction conditions: temperature (80.0°C), catalyst concentration (1.0, 2.0, 3.0, 4.0, or 5.0%), and stirring rate (400 rpm).

raw material to product. The effect of the temperature did not have much effect on the acid value as the result did not differ significantly. However, the temperature 80°C was chosen to minimize the risk of gel formation.

Figure 5 shows the hydroxyl values of the reactant with the different amounts of catalyst. Hydroxyl value decreases with the increment of the ester functionality. The hydroxyl functionality in polyol has reacted with acrylic acid to form acrylated polyol ester prepolymer. Lower hydroxyl values are obtained in syntheses that used 2.0–3.0% of catalyst. Acidic catalyst such as *p*-toluene sulfonic acid can protonate the unshared electron pairs of the oxygen in both the carboxylic acid and alcohol. At low concentration of catalyst, protonation toward the carbonyl atom of the acid is reduced. However, as esterification is an equilibrium reaction process, at higher concentration of acidic catalyst, unwanted side reaction can occur resulting in low products yield or unwanted by products. Large amount of catalyst may cause reverse reaction to occur and acid-catalyzed hydrolysis of an ester may happen.²²

In Figure 6, the acrylated polyol ester prepolymer with the highest iodine value of 12.9 g I₂/100 g was obtained by using 3.0% catalyst while the iodine value of the starting material, palm olein polyol is

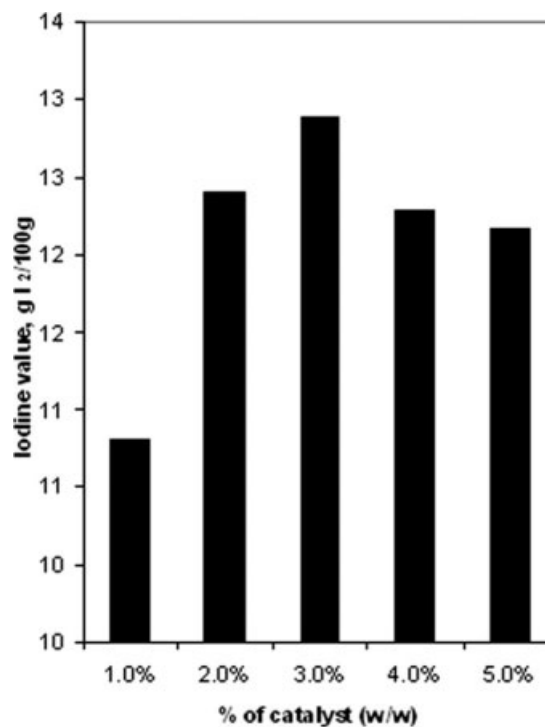


Figure 6 Iodine value for acrylated polyol ester prepolymers prepared with different amount of catalyst. Other reaction conditions: temperature (80.0°C), stirring rate (400 rpm), and reaction period (15 h).

3.6 g I₂/100 g. Higher iodine value in product is attributed to the development of vinyl group in the molecular structure. The general order of the decrement of the iodine value is 3.0% > 2.0% > 4.0% > 5.0% > 1.0%. Highest iodine value obtained for the sample synthesized using 3.0% indicating the most degree of unsaturation and favorable acrylation process in the preparation acrylated polyol ester prepolymer. The decrement of the iodine value when the concentration of the catalyst is higher than 3.0% could be due to the hydrolysis of formed ester.

FTIR spectroscopy was used to estimate the extent of acrylation by comparing the spectra of —OH peak in raw material with the acrylated polyol ester prepolymer. The result obtained is shown in Figure 7. The FTIR spectroscopy shows that the hydroxyl group is successfully converted to acetate group or acrylated functionality through condensation esterification. This is indicated from the absence of hydroxyl functionality of polyol at absorption band of 3412 cm⁻¹, associated with hydrogen bond of —OH and a strong absorption band for the carbonyl group, C=O of the polyester type polyol compound at 1737 cm⁻¹. The tiny absorption band of —OH in the acrylated prepolymers might have come from minute amount of moisture present in acrylated polyol ester prepolymer after washing and purification process. Another significantly different absorption band is observed in the spectrum at 1637 cm⁻¹ indicating the presence of vinyl functionality (—CH=CH₂—). The presence of vinyl functionality of the acrylated polyol ester prepolymer is also supported by the absorption peak at 986 cm⁻¹ as this indicates the presence of vinyl group, [CH₂=CH(CO)—O].

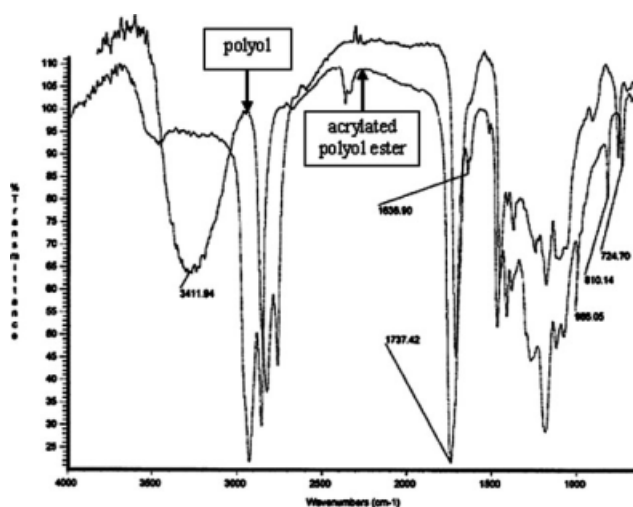


Figure 7 FTIR spectra of polyol and acrylated polyol ester prepolymer synthesized using 3.0% catalyst.

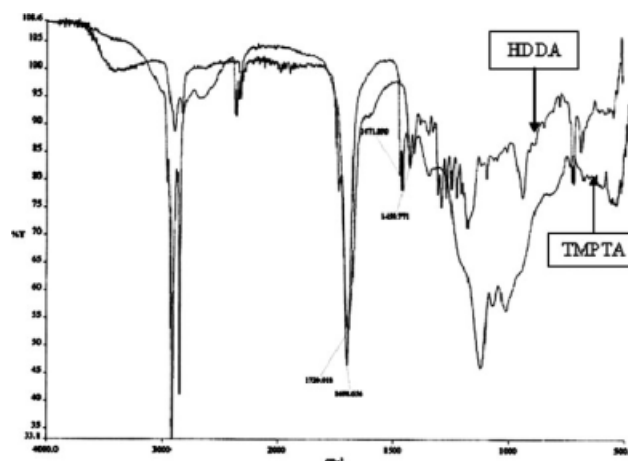


Figure 8 FTIR spectra of UV cured film after 14 passes of UV radiation (acrylated polyol ester prepolymer synthesized using 3.0% catalyst with monomer HDDA or TMPTA, 1 pass = 0.6 J/cm²).

Analysis of UV cured coating

Spectral changes and the double bond conversion that occurred within the coated materials during polymerization reaction under UV radiation are monitored. FTIR can be used to estimate the extent of UV curing by comparing FTIR spectrum of acrylated polyol ester prepolymer samples and UV cured films. The liquid–solid phase transition occurring upon UV irradiation can thus be monitored conveniently and the effects of the curing parameters can be evaluated to determine the optimum condition.

The conversion of double bond in the different cured polymers obtained from prepolymers and monomers can be seen in FTIR spectra (Fig. 8). The disappearance of the reactive double bond upon UV radiation can be followed by monitoring the infrared absorption characteristics of the carbon–carbon (C=C) double bond stretching at 1660–1600 cm⁻¹. Before UV radiation, FTIR spectrum of acrylated polyol ester prepolymer shows unsaturation at 1637 cm⁻¹. It can be seen after UV irradiation, infrared absorption characteristic of the C=C stretching at

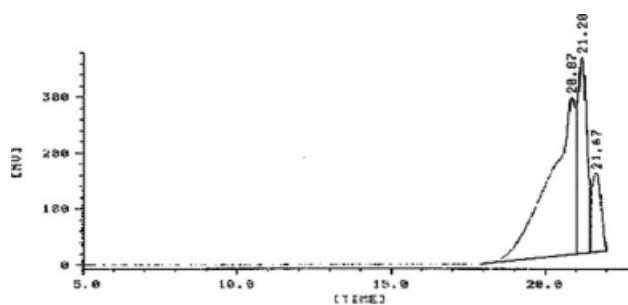


Figure 9 Gel permeation chromatography spectrum of palm olein polyol.

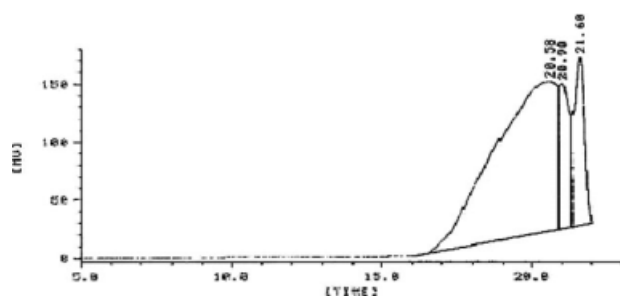


Figure 10 Gel permeation chromatography spectrum of acrylated polyol ester prepolymer synthesized using 3.0% catalyst.

around $1660\text{--}1600\text{ cm}^{-1}$ disappears although very tiny absorptions can be seen. This may be due to the presence of a certain amount of double bonds still remaining in the film substrate, perhaps from the prepared prepolymers or monomers used in the formulation. It is interpreted to mean that some residual acrylic and vinylene double bonds may be trapped and unable to react in the three-dimensional polymer matrix formed.⁸

Figures 9 and 10 show the gel permeation chromatography spectrum of palm olein polyol and acrylated polyol ester prepolymer, respectively, whereas Table II shows the weight average molecular weight (M_w), number average molecular weight (M_n), and their polydispersity index (M_w/M_n) of these samples. The weight average molecular weight (M_w) has increased because of additional acrylate functionality in polyol ester. Polydispersity index which has doubled in value indicating increased distribution of molecular masses in the prepolymer sample.

A photoinitiator (Irgacure 184) and two different monomers (HDDA or TMPTA) were used in the preparation of polymeric films with the prepared acrylated polyol ester prepolymers. The five types of prepolymers used for preparation of UV curable formulations were synthesized using 1.0, 2.0, 3.0, 4.0, or 5.0% catalyst. The Figures 11 and 12 represent the

TABLE II
Weight Average Molecular Weight (M_w), Number Average Molecular Weight (M_n), and Polydispersity Index (M_w/M_n) of Palm Olein Polyol and Acrylated Polyol Ester Prepolymer

Samples	Weight average molecular weight (M_w)	Number average molecular weight (M_n)	Polydispersity index (M_w/M_n)
Palm olein polyol	1946.8	1249.2	1.56
Acrylated polyol ester prepolymer synthesized using 3.0% catalyst	5820.3	1821.8	3.19

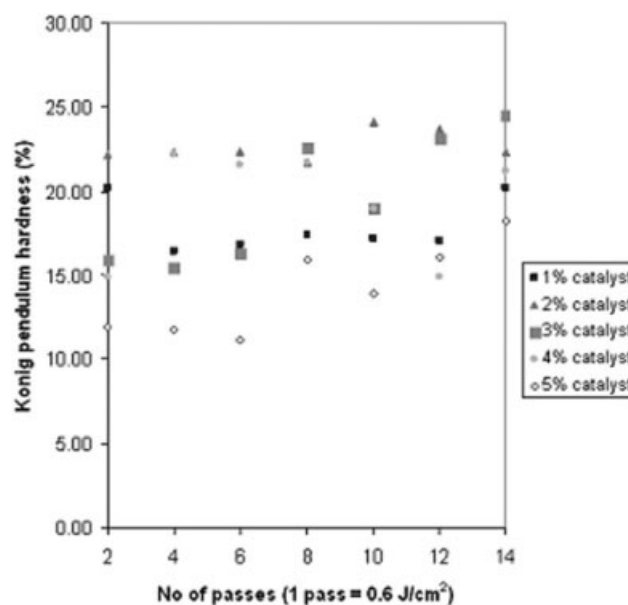


Figure 11 Effect of number of passes under UV radiation on Konig pendulum hardness of UV cured film. Formulation: HDDA monomer with prepolymers synthesized using 1.0, 2.0, 3.0, 4.0, or 5.0% catalyst.

pendulum hardness of UV-cured films prepared with HDDA or TMPTA monomer, respectively, and cured by UV radiation using different numbers of passes.

The highest Konig pendulum hardness of the UV curable polymer coating with HDDA is 24.5%, which is obtained from utilizing prepolymer synthesized using 3.0% catalyst with 14 passes of UV light

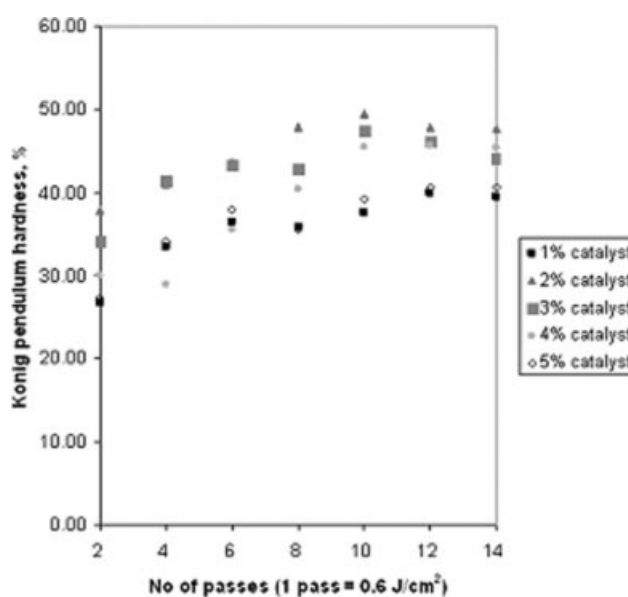


Figure 12 Effect of number of passes under UV radiation on Konig pendulum hardness of UV cured film. Formulation: TMPTA monomer with prepolymers synthesized using 1.0, 2.0, 3.0, 4.0, or 5.0% catalyst.

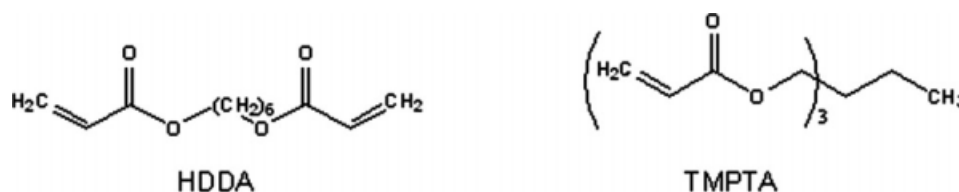


Figure 13 Structures of 1,6-hexane diol diacrylate (HDDA) and trimethylol propane triacrylate (TMPTA).

(Fig. 11). However, the usage of prepolymer synthesized using 2.0% catalyst with 10 passes of UV light yield an almost similar hardness of 24.1%. The König pendulum hardness of the UV curable polymers with TMPTA and prepolymers synthesized using 1.0, 2.0, 3.0, 4.0, or 5.0% catalyst are shown in Figure 12. The general order of pendulum hardness for formulation containing HDDA and prepolymers based on the concentration of the catalyst used in the preparation would be of 2.0% > 3.0% > 4.0% > 1.0% > 5.0% catalyst. An almost similar observation for the order of hardness can be seen for TMPTA except for prepolymer with 1.0% catalyst. The hardness of the prepolymer synthesized using 1.0% catalyst is lower than the hardness of that of 5.0% catalyst, which may be due to the monomer used. The results imply that the acrylated polyol ester prepolymer made from 3.0% catalyst which also possess the highest iodine value has more acrylate functionality and thus more suitable to be used in the UV-curable formulation.

Good König pendulum hardness for UV curable formulation with HDDA monomer is obtained when the prepolymer synthesized using 3.0% catalyst is irradiated with the dose of 14 passes. König pendulum hardness of 24.5% is obtained. However, the highest pendulum hardness of 49.4% is achieved with 10 passes when TMPTA is used with the prepolymer synthesized using 2.0% catalyst. Figure 13 shows TMPTA, which is a trifunctional monomer produces hard films with the synthesized prepolymer due to high degree of crosslinking formation. It has three double bonds which may easily form three-dimensional polymeric networks by copolymerizing with acrylic double bonds present in the synthesized prepolymers. Mono- or difunctional monomer system can be added in the formulation system to make soft or flexible films with the desired characteristics because of the linear molecular backbone of the cured films. Therefore, the pendulum hardness for the prepolymers mixed with TMPTA monomer is higher than that of the HDDA monomer.

For most of the formulations with the prepolymers, pendulum hardness is at its maximum with UV radiation up to eight passes for HDDA (Fig. 11) or 10 passes for TMPTA (Fig. 12). Continuous expo-

sure of UV radiation to the cured coating decreases pendulum hardness of some samples. Cured polymer also degraded at higher radiation.²³ This phenomenon reduces the crosslinking density, resulting in a smaller amount of gel in the films.^{24,25} In a photoinitiated polymerization reaction, once the crosslinking conversion is stopped during the termination step, polymer degradation may be initiated at higher dose of radiation.^{26,27} Alternatively, some of the reactive sites are blocked by solid network from being close enough to radicals or ions.^{19,28}

The effects of different ratios of prepolymer synthesized using 2.0% catalyst and HDDA or TMPTA monomer on pendulum hardness of cured polymeric film are shown in Figure 14. The film samples are cured using 10 passes in the UV light with strength of 0.6 J/cm² per pass. The trend is similar for both monomers. The higher the weight ratio of acrylated polyol ester prepolymer used in the formulation in

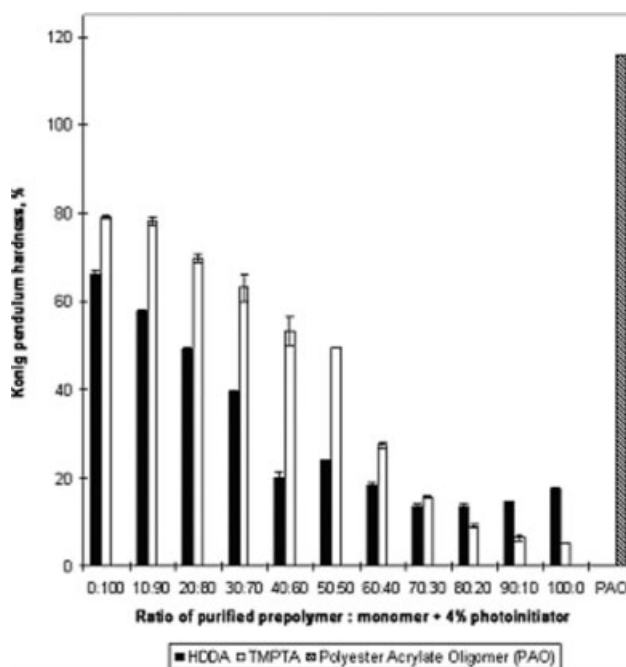


Figure 14 Effect of different ratio of prepolymer and monomers HDDA or TMPTA on König pendulum hardness of UV cured film. Formulation: prepolymer synthesized using 2.0% catalyst and number of passes under UV: 10 passes (1 pass = 0.6 J/cm²).

the film, the lower the value of Konig pendulum hardness. There is a stark difference in pendulum hardness between the commercially obtained polyester acrylate oligomer (PAO) and synthesized acrylated polyester prepolymer in Figure 14. This may be due to limited acrylate functionality of the synthesized acrylated polyol ester prepolymer from palm oil compared to the commercial monomers from petroleum sources. The limited degree of unsaturation in palm oil is restraining its capacity to be converted into useful functionalities. From the composition of the normal RBD palm olein, about 53.6% of the fatty acids present are unsaturated, which can be epoxidized, hydrolyzed and undergoes esterification with acrylic acid. The remaining 46.5% are saturated fatty acids which unfortunately do not contribute to any useful functionality in the synthesized prepolymers but the saturated portion of the triglycerides provides medium to hold the polymer network and the $-\text{CH}_2\text{CH}_3-$ groups of the end of the fatty acids chains and play a very significant role in delocalization of electrons around the double bond during free radicals production by the impact of radiation.^{29,30}

CONCLUSIONS

The suitable amount of *p*-toluene sulfonic acid monohydrate for the preparation of acrylated polyol ester prepolymer was 3.0% (w/w) based on iodine value. Acrylated polyol ester prepolymer is more suitable to use with TMPTA in formulation of radiation-curable coating application as it gave consistently good Konig pendulum hardness.

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